

Coordination Polymers with Cyanoaurate Building Blocks: Potential New Industrial Applications for Gold

Daniel B. Leznoff and Julie Lefebvre

Department of Chemistry, Simon Fraser University,
8888 University Drive, Burnaby, B.C., V5A 1S6,
CANADA. Tel: 1-604-291-4887

Fax: 1-604-291-3765 e-mail: dleznoff@sfu.ca

This report illustrates the concept that **aurophilic interactions of gold-containing building blocks, particularly cyanoaurates, could be used as a *tool* to increase structural dimensionality in systems containing *other metals* in addition to gold(I).** Such high-dimensionality systems may have useful optical, magnetic, conducting or porous materials properties. Recent successes from our group and others in using the neglected, luminescent $[\text{Au}(\text{CN})_2]^-$ building block to synthesize supramolecular coordination polymers with interesting and potentially commercially applicable physical properties will be surveyed. In most heterometallic $[\text{Au}(\text{CN})_2]$ -based polymers, aurophilic interactions increase the structural dimensionality of the system and can impart increased thermal stability. The gold(I) ion can mediate significant magnetic interactions between transition-metal centres or influence iron(II) spin-transition behaviour in the polymers. The $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{solvent})_x$ polymer system is dynamically vapochromic, i.e., it shows large, reversible colour changes upon exposure to solvent vapours, thereby illustrating a sensor-type application. The related d^8 , square-planar $[\text{Au}(\text{CN})_4]^-$ building block, which has only recently been incorporated into coordination polymers, does not form any aurophilic interactions; weak Au-N(cyano) interactions control the intermolecular packing. Several structural examples of cyanoaurate-based coordination polymers are presented, including 2-D and 3-D arrays. The incorporation of cyanoaurates as components of advanced materials would provide a new utility and market for these key compounds of the gold mining and refining industry.

Introduction

Research into the chemistry of supramolecular coordination polymers has rapidly grown in recent years due to an increased demand for functional materials with tunable conductive, magnetic, non-linear optical or zeolitic properties (1,2). This focus on coordination polymers stems from the fact that the generation of many such properties is enhanced by, or depends on, the synthesis of high-dimensionality materials. The self-assembly of simple molecular building blocks containing organic ligands and inorganic metal ions using a combination of metal-ligand coordinate bonding, hydrogen-bonding or π - π interactions is a common route to generating high dimensionality organic-inorganic hybrid materials (1,3). The characteristics of the inorganic and organic moieties, such as available coordination sites, coordination geometry preference, ligand flexibility, and presence or absence of hydrogen-bonding or π - π stacking groups, ideally control the extended structure, thereby creating enormous potential for complexity and functionality of these modular materials (1,3).

To reiterate, one of the key requirements for generating functional materials by self-assembly is the ability to rationally increase structural dimensionality. The addition of hydrogen-bonding groups into the organic portion of the material to induce intermolecular interactions is a widespread technique for achieving this goal (4). As readers of *Gold Bulletin* are aware (5), gold has special chemical properties, one of which is the propensity of d^{10} gold(I) ions to be attracted to each other; this effect has been termed “*aurophilic interactions*” (6). These attractive aurophilic interactions have an order-of-magnitude strength similar to hydrogen-bonding (6), and many homometallic gold(I) polymers generated by aurophilic interactions alone, or in conjunction with hydrogen-bonding organic moieties, have been reported (5-7). However, the concept that aurophilic interactions could be used (like hydrogen-bonding) as a *tool* to increase dimensionality in systems containing *other metals* in addition to gold(I) had not been seriously considered and we turned our attention to this design question (8).

The building block dicyanoaurate, $d^{10} [\text{Au}(\text{CN})_2]^-$, is an ideal unit with which to explore the use of aurophilicity as a supramolecular design element in the synthesis of such *heterometallic* coordination polymers. In general, cyanometallate building blocks, $[\text{M}(\text{CN})_x]^{n-}$ have been extensively utilized to form multidimensional networks (9) because both the carbon and the nitrogen ends of the cyanide ion act as Lewis bases that can coordinate two different metal cations acting as the corresponding Lewis acids (i.e. M-CN-M' , Scheme 1). Accordingly, cyanometallates readily form coordination polymers when reacted with transition-metal cations and can promote strong magnetic exchange. Also, the $\text{C}\equiv\text{N}$ vibrational stretch in the IR is a very sensitive, diagnostic probe (10). However, most studies have focused on octahedral $[\text{M}(\text{CN})_6]^{n-}$ and, to a lesser extent, square-planar $[\text{M}(\text{CN})_4]^{n-}$ bridging units. Until recently, the

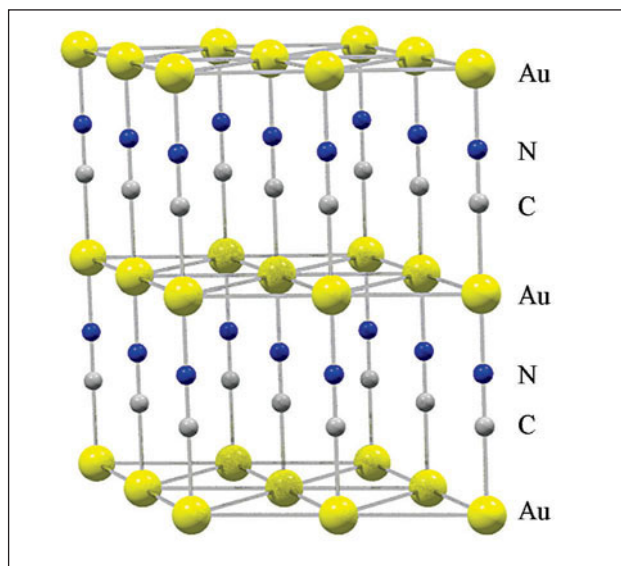
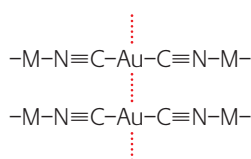


Figure 1
Solid-state structure of AuCN

linear $[\text{Au}(\text{CN})_2]^-$ cyanometallate anion (a key material in gold extraction (11)) had never been used as a building block in supramolecular coordination chemistry despite its special ability among cyanometallates to form aurophilic interactions. In addition, $[\text{Au}(\text{CN})_2]^-$ salts are known to have luminescent properties (12-13) and in principle, coordination polymers assembled using cyanoaurate building blocks may retain this useful material property.

These principles can all be illustrated by examining the simple salt AuCN. Despite the straightforward chemical formula, in the solid state AuCN forms a complex 3-D polymer (Figure 1), with chains of $-\text{Au-CN-Au-CN}-$ atoms (in which the cyanide is acting as both a C- and an N-donor to two gold(I) centres) connected by Au-Au interactions of 3.396 (2) Å (14). The structure could also be viewed as 2-D sheets of hexagonally arranged gold(I) atoms that are connected by cyanide ligands. The strong aurophilic interactions are preserved in a series of related chain- or sheet-polymeric (alkyl isocyanide)AuCN complexes (15) and chain-polymeric (trimethylphosphine)AuCN (16), which have structures reminiscent of portions of the parent AuCN. These AuCN-based complexes all show significant luminescence in the solid-state, as would be expected from the presence of aurophilic interactions. Interestingly, salts of $[\text{Au}(\text{CN})_2]^-$ with organic cations show aurophilic interactions and concomitant luminescence only when the cations have hydrogen-bonding moieties incorporated (13,17). The



Scheme 1
The dicyanoaurate building block can form both M-N bonds and aurophilic interactions

structures of the “simple” alkali-metal salts $\text{M}[\text{Au}(\text{CN})_2]$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) also have similarities with the AuCN structure: layers of $[\text{Au}(\text{CN})_2]^-$ anions separated by and ligated to layers of alkali-cations, with the cyanoaurate units showing varying degrees of aurophilicity within the gold-containing plane (18). These features of AuCN-based structural chemistry highlight the underlying interest in exploring cyanoaurates as building blocks in heterometallic polymers.

Thus, with the above concepts in mind, we set out to explore the question of whether $[\text{Au}(\text{CN})_2]^-$ -based coordination polymers could be prepared and whether their structural dimensionality would be increased by aurophilic interactions (Scheme 1) (8,19,20). What unusual structural motifs could be generated using these gold-containing units? What unique physical properties could be built into the resulting cyanoaurate-based polymers and what applications could be envisaged? As a comparison, we have also been exploring the use of the electronically and structurally related linear, anionic d^{10} $[\text{Ag}(\text{CN})_2]^-$ (21) and linear, neutral d^{10} $\text{Hg}(\text{CN})_2$ (22) as building blocks for heterometallic coordination polymers. These investigations clearly illustrate that gold truly is special: the mode of reactivity and the structures and stability of the polymers that form with cyanoaurate differ significantly compared to the silver and mercury units. As a further comparison with the d^{10} $[\text{Au}(\text{CN})_2]^-$ building block, we have also investigated the use of square-planar d^8 $[\text{Au}(\text{CN})_4]^-$ -containing coordination polymers (23). This article outlines some progress in this new area of gold-research, and attempts to address the above questions.

Dicyanoaurate $[\text{Au}(\text{CN})_2]^-$ as a building block: Structural and magnetic properties

One example of the use of dicyanoaurate to self-assemble high-dimensionality coordination polymers is the reaction of a divalent transition metal salt MX_2 ($\text{X} = \text{ClO}_4, \text{NO}_3$ etc.), pyrazine and $\text{KAu}(\text{CN})_2$ to give $\text{M}(\text{pyrazine})[\text{Au}(\text{CN})_2]_2$ complexes ($\text{M} = \text{Cu}, \text{Ni}, \text{Co}, \text{Mn}$) (19). The copper(II) analogue was structurally characterized (Figure 2, left) as a 3-D system with chains of $\text{Cu}(\text{II})$ -pyrazine moieties in the *a* direction, connected by $[\text{Au}(\text{CN})_2]$ bridges. Alternatively, the structure could be considered to be constructed of $\text{Cu}[\text{Au}(\text{CN})_2]_2$ planes that are connected by pyrazine bridges. The 3-D network is not porous, despite the appearance to the contrary, as a second identical network interpenetrates the first to fill the space (Figure 2, right). The two networks are connected via weak aurophilic interactions of 3.4729(2) Å, which is less than 3.6 Å, the sum of the van der Waals radii of two gold atoms and the accepted limit for such interactions (6). The thermal decomposition temperatures of these polymers, as determined by thermogravimetric analysis, are unusually high: up to 406°C for the Ni-analogue. This high thermal stability can be attributed to the Au-Au interactions that reinforce the polymer

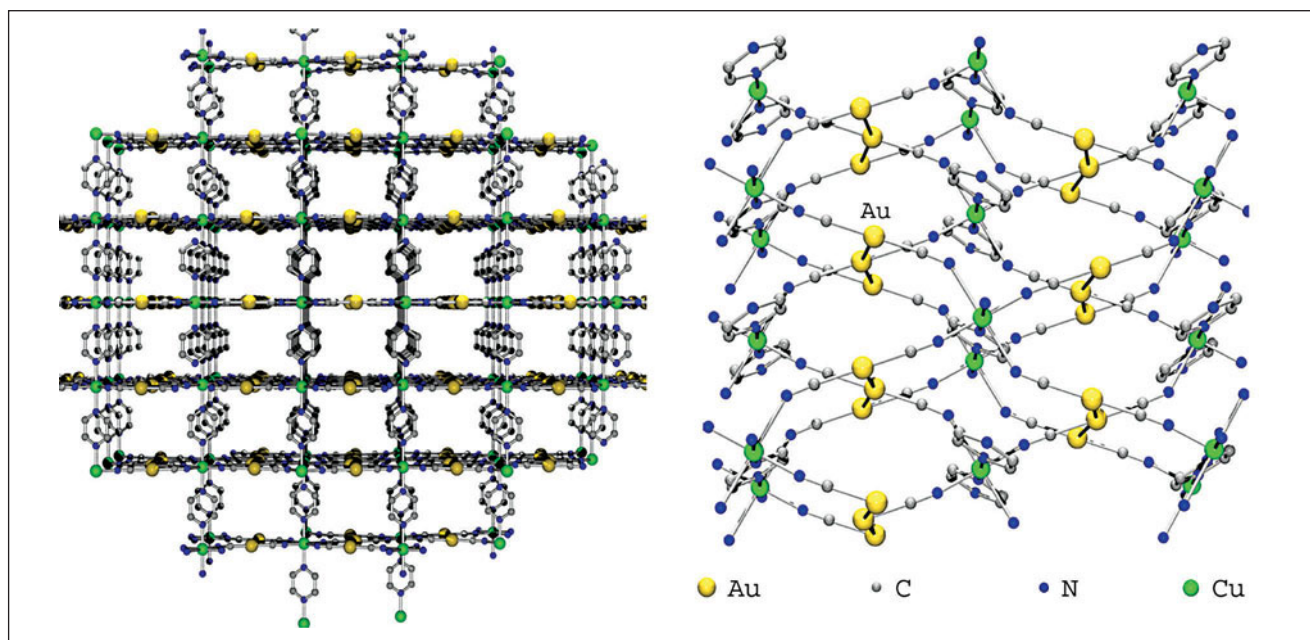


Figure 2

Extended 3-D structure of one network of $\text{Cu}(\text{pyrazine})[\text{Au}(\text{CN})_2]_2$ (left) and interpenetrating networks supported by Au-Au interactions (right)

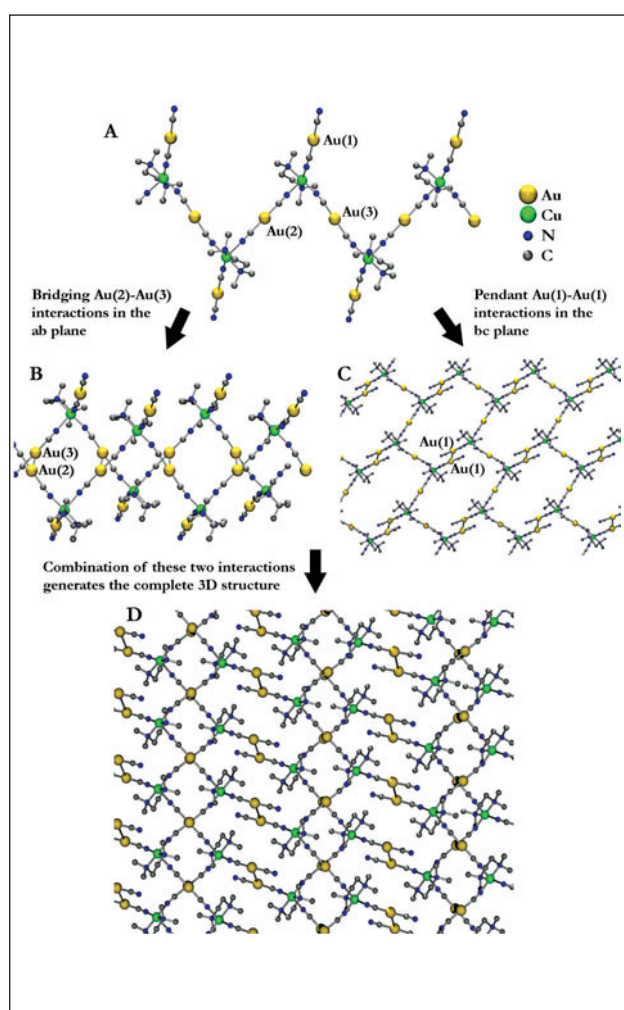


Figure 3

Starting with the 1-D chain structure of $(\text{tmeda})\text{Cu}[\text{Au}(\text{CN})_2]_2$, considering (a) solely the metal-ligand coordinate bonds, (b,c) the additional consideration of the gold-gold interactions in each plane yields the true 3-D structure (d), as viewed down the *a*-axis

superstructure. Thus, although in this initial case the introduction of aurophilic interactions did not increase the structural dimensionality, the physical properties were positively influenced.

The goal of using aurophilic interactions as a tool to increase dimensionality was achieved from the reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, tmeda (N,N,N',N' -tetramethylethylenediamine) and $\text{KAu}(\text{CN})_2$ in water, yielding $(\text{tmeda})\text{Cu}[\text{Au}(\text{CN})_2]_2$ (8). By virtue of metal-ligand coordinate bonds, this system is a 1-D chain (Fig. 3a), containing both copper(II)-bridging and -pendant $[\text{Au}(\text{CN})_2]$ units. However, each gold centre also forms Au-Au interactions thereby increasing the structural dimensionality. Thus, the Au(2) and Au(3) atoms in the backbone of the 1-D chain form interchain Au-Au interactions of 3.5378(8) Å to yield a 2-D array of alternating 1-D zig-zag chains in the *ab* plane (Figure 3b). The pendant Au(1) atoms also form Au(1)-Au(1) interactions of 3.345(1) Å to adjacent chains in the *bc* plane (Figure 3c),

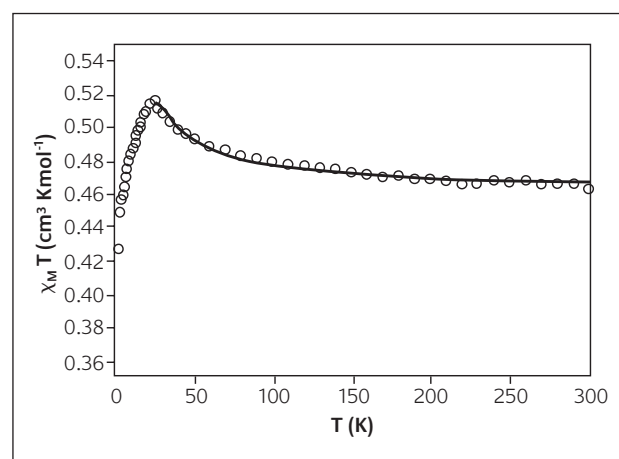


Figure 4

Ferromagnetic (above 25 K) behaviour of $(\text{tmeda})\text{Cu}[\text{Au}(\text{CN})_2]_2$

yielding a ladder-rung type motif running parallel to the 1-D chains. Taken together, the complete 3-D picture of the structure is shown in Figure 3d. The Au-Au interactions have increased the structural dimensionality from one to three. Several other heterometallic cyanoaurate polymers where Au-Au interactions play an important role can be found in the literature (24-27).

The structures shown in Figures 2 and 3 illustrate a noteworthy feature present in many $[\text{Au}(\text{CN})_2]$ -containing polymers: adjacent cyanoaurate anions can form aurophilic interactions with the relative orientation of the two NCAuCN units ranging from completely eclipsed (a 0° dihedral angle) to completely staggered (90°). Thus, in $(\text{tmeda})\text{Cu}[\text{Au}(\text{CN})_2]_2$, the Au(2) and Au(3)-containing cyanoaurate units are nearly staggered (81.8° dihedral angle, Fig. 3b) while the ladder-rung motif units are nearly eclipsed (2.5° dihedral angle, Fig. 3c). In $\text{M}(\text{pyrazine})[\text{Au}(\text{CN})_2]_2$, the interpenetrated networks of cyanoaurate anions (Fig. 2, right) are 36.1° twisted relative to each other. Detailed discussions of this structural feature in a variety of cyanoaurate(I) systems have been published (17,20). In addition, a theoretical analysis of the energetically preferred orientation of two cyanoaurate ions as a function of Au-Au distance showed that, with the presence of aurophilic interactions, the fully staggered 90° arrangement is energetically stabilized relative to the eclipsed conformation (28).

The polymer $(\text{tmeda})\text{Cu}[\text{Au}(\text{CN})_2]_2$ also has an unusual physical property: ferromagnetic coupling of the copper(II) spins. As shown in Figure 4, the magnetic moment ($\chi_{\text{M}}T$) increases as the temperature is lowered to 25 K, indicative of ferromagnetic interactions; these are propagated by the diamagnetic $[\text{Au}(\text{CN})_2]$ bridges. To our knowledge, this is the first example of a gold(I) atom mediating any magnetic interactions. Ferromagnetic interactions in particular are of interest in the design of molecule-based magnetic materials (2).

Another important magnetic property that is being targeted by coordination polymer materials is spin-transition. Such materials, usually containing iron(II) metal centres, have the ability to switch their magnetic state between high- and low-spin as a function of temperature, pressure or light excitation, and have potential applications as sensors or memory-storage devices (26). A series of $[\text{Au}(\text{CN})_2]$ -based coordination polymers containing iron(II) centres has been reported and they show interesting spin-transition behaviour. In addition to the cyanoaurate acting as a bridging building block, in some of these systems, aurophilic interactions serve to hold multiple networks together, and also influence the magnetic spin-transition properties (27).

Recently, an $[\text{Au}(\text{CN})_2]$ -containing cobalt(II) complex that also incorporates the stable organic radical pyridylnitronyl nitroxide has been reported; this material polymerizes via both Au-Au and hydrogen bonding interactions, but the magnetic properties do not appear to be influenced by the gold(I) centre (29). Materials that contain both gold centres and a stable organic radical are rare (30).

Vapochromic Gold(I)-containing Coordination Polymers

Vapochromic materials, which display optical absorption or luminescence changes upon exposure to vapours of volatile organic compounds (VOCs), have been a focus of attention due to their potential applications as chemical sensors. Several vapochromic compounds based on Au(I)-coordination polymers have been recently reported (31-34). In the linear $\{\text{Ti}[\text{Au}(\text{C}_6\text{Cl}_5)_2]\}_n$ polymer, weak interactions between the Ti atoms and the adsorbed VOC molecules

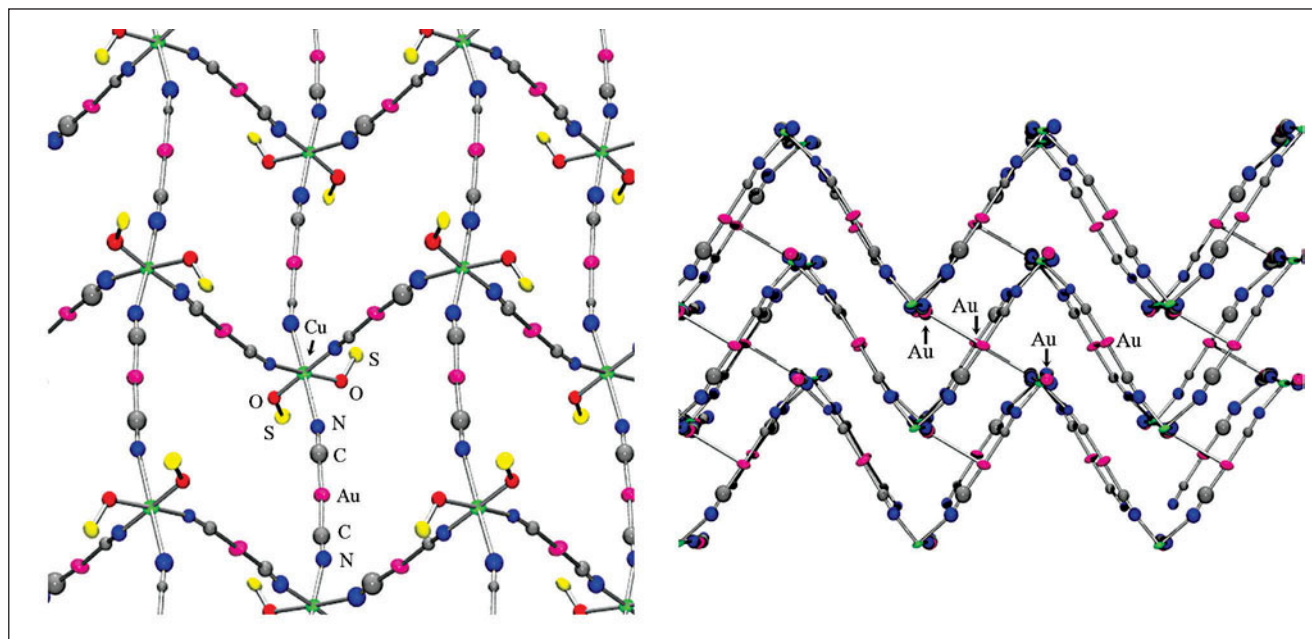


Figure 5

Structural depiction of the blue polymorph of $\text{Cu}(\text{DMSO})_2[\text{Au}(\text{CN})_2]_2$, top view on left and side-view on right. DMSO molecules simplified (left) or removed (right) for clarity. Note the gold-gold bonding between the corrugated sheets

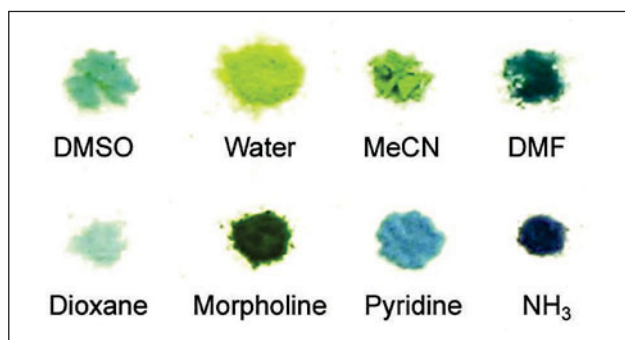


Figure 6

Colour changes with donor-solvent vapour on the solid $\text{Cu}(\text{DMSO})_2[\text{Au}(\text{CN})_2]_2$

modify both the colour and the emission spectra (32). Another example is the trinuclear Au(I) complex with carbenate bridging ligands, for which its luminescence is quenched in the solid-state when C_6F_6 vapour is adsorbed due to the disruption of Au-Au interactions (33). Also, $[\text{Au}(\text{PPh}_2\text{C}(\text{CSSAuC}_6\text{F}_5)\text{PPh}_2\text{Me})_2][\text{ClO}_4]$ has been used in the development of an optical fibre volatile organic compound sensor (34).

In this context, we have prepared a series of $[\text{Au}(\text{CN})_2]$ -based coordination polymers that show reversible vapochromic behaviour (35). The structures described above utilized a chelating amine to selectively block two or more sites of reactivity at the transition-metal. Removal of these ancillary ligands allows for solvent-sensitive products to form. Thus, reaction of a copper(II) salt with $\text{KAu}(\text{CN})_2$ in dimethylsulfoxide (DMSO) solvent yields $\text{Cu}(\text{DMSO})_2[\text{Au}(\text{CN})_2]_2$, where the DMSO solvent has been incorporated into the structure. In fact, there are two polymorphs (same molecular units, but different supramolecular arrangement of the building blocks) of this system, one of which is green and the other of which is blue. The X-ray crystal structure of the blue polymorph, for example, reveals that the copper(II) centre adopts a distorted octahedral geometry, where the two DMSO molecules are bound in a cis fashion. The four remaining sites around the

copper(II) centre are occupied by cyano-nitrogen atoms of bridging $[\text{Au}(\text{CN})_2]$ units, thereby generating 2-D sheets (Figure 5, left). The corrugated sheets stack (Figure 5, right) to form a 3-D network that is held together via weak Au-Au interactions of 3.426(4) Å.

When exposing the $\text{Cu}(\text{DMSO})_2[\text{Au}(\text{CN})_2]_2$ material to vapours of other volatile solvents, significant colour changes result (i.e. the system is vapochromic), indicating that replacement of DMSO for the solvent vapours has occurred. Each $\text{Cu}[\text{Au}(\text{CN})_2]_2(\text{solvent})_x$ complex can be distinguished easily by its colour (Figure 6). In addition, the ν_{CN} region of the IR spectrum for each solvent complex is a characteristic, sensitive signature for that solvent. Importantly, this solvent exchange is completely reversible, thus permitting dynamic solvent sensing; a variety of solvents, including water, acetonitrile, dimethylformamide and dioxane can all be reversibly detected both via visible colour changes and the changes in the IR-spectrum. Very strong donor solvents such as pyridine or ammonia, which bind strongly to the copper(II) centre and are not easily displaced by other solvents, require a thermal treatment to regenerate the vapochromic behaviour. In general, this is a successful illustration of a cyanogold-based sensor for volatile organic compounds (35). We have also prepared the related $\text{M}[\text{Au}(\text{CN})_2]_2$ systems (M = 1st row transition metal) and are exploring their potential materials applications.

These gold-containing vapochromic sensor materials have a variety of potential applications. For example, the material could form the basis of personal badge or stationary threshold monitors in chemical laboratories (e.g. pharmaceutical research laboratories, paint and coatings or cosmetics manufacturing) or storage facilities for hazardous vapour detection or regulated emission requirements. Similarly, an environmental sensor for volatile organic compounds or gases ("electronic noses") for use at environmental remediation sites, landfills, air-quality monitoring etc. could potentially be developed with the gold-based vapochromic material at the heart of the device.

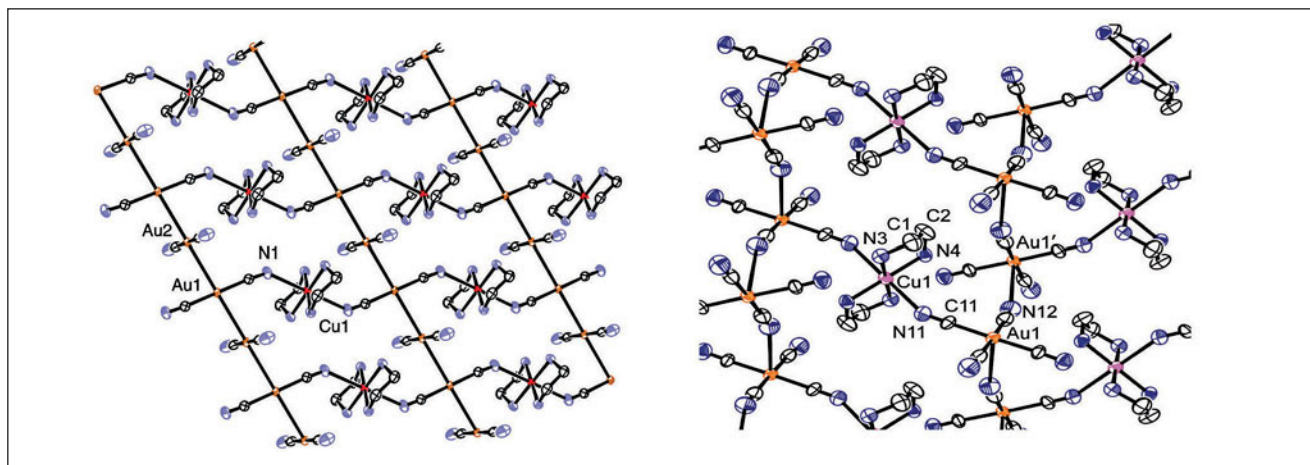


Figure 7

2-D structures of $\text{Cu}(\text{en})_2[\text{Au}(\text{CN})_2]_2$ (left) and $\text{Cu}(\text{en})_2[\text{Au}(\text{CN})_4]_2$ (right)

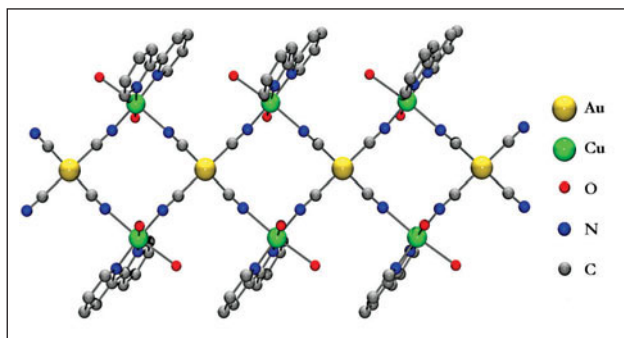


Figure 8

1-D chain structure of the cation of $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2(\text{Au}(\text{CN})_4)_{0.5}][\text{Au}(\text{CN})_4]_{1.5}$

Tetracyanoaurate(III) as a building block

Prior to our recent studies, there were no reported coordination polymers of the d^8 cyanometallate $[\text{Au}(\text{CN})_4]^-$ and only the simple $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ (36) and $\text{KAu}(\text{CN})_4(\text{H}_2\text{O})$ (37) salts had been structurally characterized. As a comparison with d^{10} $[\text{Au}(\text{CN})_2]^-$, which forms aurophilic interactions, and d^8 $[\text{Pt}(\text{CN})_4]^{2-}$, which forms Pt-Pt stacks (38), we prepared a series of $[\text{Au}(\text{CN})_4]$ -containing coordination polymers (23), using the same transition-metal amine cations as for the dicyanoaurate studies, and new structural motifs were identified. Since some 1-D Pt-Pt chains show strong conductivity, luminescence and electronic delocalization, it is important to determine if such properties can be accessed with isoelectronic $\text{Au}(\text{III})$.

To summarize the findings, d^8 $[\text{Au}(\text{CN})_4]^-$ is a weaker ligand than the $\text{Au}(\text{I})$ or $\text{Pt}(\text{II})$ counterparts but still yields polymers via M-NC coordinate bonds and also by an interaction

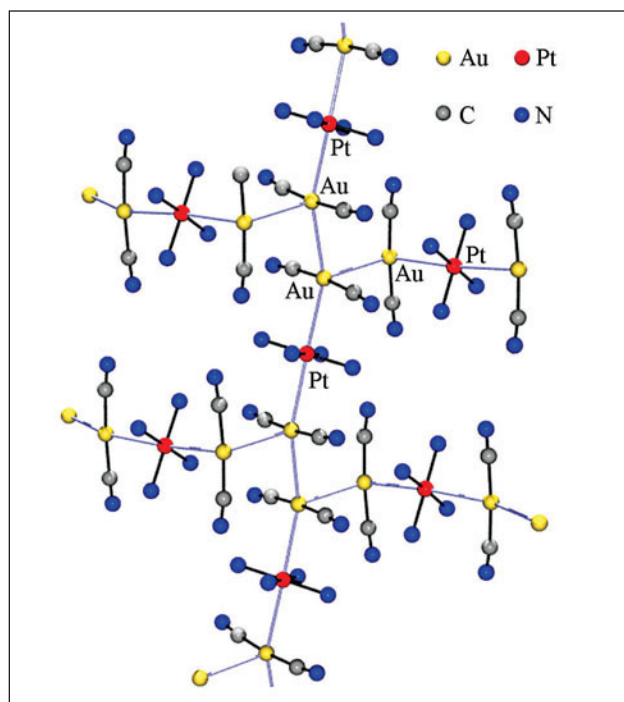


Figure 9

2-D array of $[\text{Pt}(\text{NH}_3)_4][\text{Au}(\text{CN})_2]_2$ assembled via $\text{Pt}(\text{II})$ - $\text{Au}(\text{I})$ and $\text{Au}(\text{I})$ - $\text{Au}(\text{I})$ interactions

observed for the first time: weak $\text{Au}\cdots\text{N}(\text{cyano})$ intermolecular contacts in the axial position of $[\text{Au}(\text{CN})_4]^-$. No aurophilic interactions are observed at all - in the systems prepared to date, no $\text{Au}(\text{III})$ -stacking analogous to the $\text{Pt}(\text{II})$ stacking occurred. These generalizations are exemplified by the $\text{Cu}(\text{en})_2[\text{Au}(\text{CN})_x]_2$ system (en = ethylenediamine), which was prepared with both $\text{Au}(\text{I})$ ($x=2$) and $\text{Au}(\text{III})$ ($x=4$) building blocks. The $[\text{Au}(\text{CN})_2]$ -based system (Fig. 7, left) forms a 1-D chain by virtue of M-NC coordinate bonding in the axial position of copper(II) and these chains are connected into a 2-D array by strong $\text{Au}(\text{I})$ - $\text{Au}(\text{I})$ bonding of 3.1405(2) Å (20). By comparison, the $[\text{Au}(\text{CN})_4]$ -based system is molecular unless the weak $\text{Au}(\text{I})\cdots\text{N}(\text{12,cyano})$ interactions of 3.035(8) Å are included, thereby yielding a 2-D array (Fig. 7, right) (23).

In another example, $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2(\text{Au}(\text{CN})_4)_{0.5}][\text{Au}(\text{CN})_4]_{1.5}$ forms a 1D "criss-crossed" chain where one $[\text{Au}(\text{CN})_4]^-$ bridges four $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2]^{2+}$ centres (Figure 8); the other $[\text{Au}(\text{CN})_4]^-$ units aggregate into trimeric anionic clusters via $\text{Au}\cdots\text{NC}$ interactions (23). Replacing the cyanaurate(III) unit with $[\text{Pt}(\text{CN})_4]^{2-}$ in the synthesis gives rise to a completely different structure. When $[\text{Pt}(\text{CN})_4]^{2-}$ reacts with $[\text{Cu}(\text{bipy})]^{2+}$ in water, discrete molecular squares of $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})(\text{Pt}(\text{CN})_4)]_2 \cdot 2\text{H}_2\text{O}$ are obtained (39). However, if the reaction is performed in methanol, a 2-D layered structure, $[\text{Cu}(\text{bipy})(\text{Pt}(\text{CN})_4)]$, is obtained (40). On a similar note, in the reaction of $\{[\text{Ni}(\text{dien})(\text{H}_2\text{O})]_2(\mu\text{-oxalate})\}^{2+}$ with $\text{KAu}(\text{CN})_4$, the only other reported coordination polymer with tetracyanoaurate is formed, in which a chain of $\text{Ni}(\text{II})$ -dimers is connected by an interesting combination of Ni - NCAu coordinate bonding and intermolecular amino $\text{N-H}\cdots\text{NCAu}$ hydrogen bonding (41). The analogous reaction with $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M}=\text{Ni}, \text{Pd}, \text{Pt}$) gives trimetallic Ni_2M species in which the cyanometallate bridges the two nickel centres of the dimer in an intramolecular fashion; no polymer is formed (41).

Related to this search for d^8 - d^8 $\text{Au}(\text{III})$ - $\text{Au}(\text{III})$ stacking interactions, a d^8 - d^{10} $\text{Pt}(\text{II})$ - $\text{Au}(\text{I})$ chain was recently prepared, using $[\text{Pt}(\text{NH}_3)_4]^{2+}$ cations and $[\text{Au}(\text{CN})_2]^-$ anions (25). The structure is a 2-D array formed primarily by metal-metal bonds, with $\text{Pt}(\text{II})$ - $\text{Au}(\text{I})$ bonds of 3.2794(4) Å in one direction and $\text{Au}(\text{I})$ - $\text{Au}(\text{I})$ bonds ranging from 3.1902(5) to 3.3312(5) Å in two dimensions (see Figure 9). This gold/platinum coordination polymer is luminescent at 443 nm when cooled.

Conclusions and Future Prospects

It has become clear that d^{10} $[\text{Au}(\text{CN})_2]^-$ and, to a lesser extent, d^8 $[\text{Au}(\text{CN})_4]^-$ are viable building blocks to form heterometallic coordination polymers. Both systems can be used to increase structural dimensionality, using gold-gold and gold-N(cyano) interactions respectively, beyond the metal-ligand coordinate bond framework. Physical properties such as thermal stability, magnetic coupling and spin-transition behaviour can also be influenced. More research should yield information on how to predict

and control the nature of the structures produced, given a specific metal/ligand combination. The discovery of reversible vapoehromic behaviour in a series of $[\text{Au}(\text{CN})_2]^-$ -based polymers is a strong indication that potentially commercial properties can be accessed. Thus, the luminescence of $[\text{Au}(\text{CN})_2]^-$, the potential conductivity of $[\text{Au}(\text{CN})_4]^-$ stacks (as yet unobserved), zeolitic, and non-linear optical properties of gold-containing heterometallic coordination polymers all provide impetus for further exploration of possible applications of these systems. The incorporation of cyanoaurates as components of advanced materials would provide a new utility and market for these key compounds of the gold mining and refining industry.

Acknowledgements

We are grateful to the World Gold Council GROW programme and the Natural Sciences and Engineering Council of Canada (NSERC) for supporting this research.

About the Authors

Dr. Daniel Leznoff completed his Ph.D. degree with Professor Michael Fryzuk in 1997 at the University of British Columbia (Vancouver, Canada). He was an NSERC Postdoctoral Fellow from 1997-1999 at the Bordeaux Institute for Condensed Matter Chemistry (ICMCB-CNRS) under the supervision of Professor Olivier Kahn. In 1999 he joined the Chemistry Department at Simon Fraser University (Burnaby, Canada), where he is now Associate Professor. His interests include the synthesis and characterization of gold and silver-containing heterometallic coordination polymers for materials applications, paramagnetic organometallic chemistry and actinide chemistry.

Julie Lefebvre is currently a Ph.D. student in the Department of Chemistry at Simon Fraser University. She received her B.Sc. degree in chemistry from McGill University (Montreal, Canada) in 2003. Her thesis research, under the direction of D.B. Leznoff, focuses on the preparation and characterization of $[\text{Au}(\text{CN})_2]^-$ -based heterometallic coordination polymers that show vapoehromic, magnetic or luminescent properties. She was the recipient of the "Placer Dome Best Student Presentation" award at the Gold 2003 Conference held in Vancouver.

References

- 1 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2003, 2781; L. Ouahab, *Chem. Mater.*, 1997, **9**, 1909
- 2 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark and A.E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115; J.S. Miller, *Inorg. Chem.*, 2000, **39**, 4392; O. Kahn, *Magnetism: A Supramolecular Function*, Kluwer Academic Publishers, Dordrecht, 1996; S. Decurtins, R. Pellaux, G. Antorrena and F. Palacio, *Coord. Chem. Rev.*, 1999, **190-192**, 841; D.M. Roundhill and J.P. Fackler, Jr., *Optoelectronic Properties of Inorganic Compounds*, Plenum Press, New York, 1999; M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe and O.M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319
- 3 S. Kitagawa, R. Kitaura, and S.-I. Noro, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 2334; D.J. Chesnut, D. Hargman, P.J. Zapf, R.P. Hammond, R. LaDuca, R.C. Haushalter and J. Zubieta, *Coord. Chem. Rev.*, 1999, **192**, 737
- 4 B. Moulton and M.J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; D. Braga, F. Grepioni and G.R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375
- 5 W.S. Rapsom, *Gold Bull.*, 1989, **22**, 19; H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3; E.J. Fernández, A. Laguna and J.M. López-de-Luzuriaga, *Gold Bull.*, 2001, **34**, 14; A.L. Balch, *Gold Bull.*, 2004, **37**, 45
- 6 R.J. Puddephatt, *Coord. Chem. Rev.*, 2001, **216**, 313; H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391; P. Pykkö, *Chem. Rev.*, 1997, **97**, 597; M. Bardaji and A. Laguna, *J. Chem. Educ.*, 1999, **76**, 201
- 7 A. Codina, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, J. Pérez and M.A. Rodríguez, *J. Am. Chem. Soc.*, 2002, **124**, 6781; C. Hollatz, A. Schier and H. Schmidbaur, *J. Am. Chem. Soc.*, 1997, **119**, 8115; B.C. Tzeng, A. Schier, H. Schmidbaur, *Inorg. Chem.*, 1999, **38**, 3978; B. Arhens, P.G. Jones, A.K. Fischer, *Eur. J. Inorg. Chem.*, 1999, 1103
- 8 D.B. Leznoff, B.-Y. Xue, B.O. Patrick, V. Sanchez and R.C. Thompson, *J. Chem. Soc., Chem. Commun.* 2001, 259
- 9 T. Iwamoto, In *Comprehensive Supramolecular Chemistry*, J.M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vogtle and G.T.B. Alberti, Eds., 1996, Vol. 6, 643; J. Cernak, M. Orendac, I. Potocnak, J. Chomic, A. Orendacova, J. Skorsepa, and A. Feher, *Coord. Chem. Rev.*, 2002, **224**, 51; M. Ohba and H. Okawa, *Coord. Chem. Rev.*, 2000, **198**, 313; M. Verdager, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scullier, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier and F. Villain, *Coord. Chem. Rev.*, 1999, **190-192**, 1023
- 10 K.R. Dunbar and R.A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283; J. Lefebvre and D.B. Leznoff, In *Metal and Metalloid-containing Polymers*, Vol. 6, Wiley, 2005, in press
- 11 *Gold: Progress in Chemistry, Biochemistry, and Technology*, H. Schmidbaur Ed., New York, Wiley, 1999
- 12 M.A. Rawashdeh-Omary, M.A. Omary, H.H. Patterson and J.P. Fackler, Jr., *J. Am. Chem. Soc.*, 2001, **123**, 11237; M.A. Rawashdeh-Omary, M.A. Omary and H.H. Patterson, *J. Am. Chem. Soc.*, 2000, **122**, 10371
- 13 M. Stender, M.M. Olmstead, A.L. Balch, D. Rios and S. Attar, *J. Chem. Soc., Dalton Trans.*, 2003, 4282
- 14 G.S. Zhdanov and E.A. Shugam, *Acta Physicochimica URSS*, 1945, **20**, 253; G.A. Bowmaker, B.J. Kennedy and J.C. Reid, *Inorg. Chem.*, 1998, **37**, 3968
- 15 S. Esperas, *Acta Chem. Scand.*, 1976, **A30**, 527; R.L. White-Morris, M. Stender, D.S. Tinti, A.L. Balch, D. Rios, S. Attar, *Inorg. Chem.*, 2003, **42**, 3237
- 16 S. Ahrland, B. Aurivillius, K. Dreisch, B. Norén, A. Oskarsson, *Acta Chem. Scand.*, 1992, **46**, 262
- 17 R.E. Cramer, D.W. Smith and W. VanDoorne, *Inorg. Chem.*, 1998, **37**, 5895; R.Y. Liao, H. Ehlich, A. Schier, H. Schmidbaur, *Z. Natur.*, 2002, **B57**, 1085

- 18 N. Blom, A. Ludi, H.-B. Bürgi, K. Tichy, *Acta Crystallogr.*, 1984, **C40**, 1767; N. Blom, A. Ludi and H.-B. Bürgi, *Acta Crystallogr.*, 1984, **C40**, 1770; A. Rosenzweig, D.T. Cromer, *Acta Crystallogr.*, 1959, **12**, 709; M.S. Hussain, A.R. Al-Arfaj, M.N. Akhtar, A.A. Isab, *Polyhedron*, 1996, **15**, 2781; R.J. Schubert and K.J. Range, *Z. Natur.*, 1990, **B45**, 629
- 19 D.B. Leznoff, B.-Y. Xue, C.L. Stevens, A. Storr, R.C. Thompson and B.O. Patrick, *Polyhedron*, 2001, **20**, 1247
- 20 D.B. Leznoff, B.-Y. Xue, R.J. Batchelor, F.W.B. Einstein and B.O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026 and references therein
- 21 C.J. Shorrock, B.-Y. Xue, P.B. Kim, R.J. Batchelor, B.O. Patrick and D.B. Leznoff, *Inorg. Chem.*, 2002, **41**, 6743
- 22 N.D. Draper, R.J. Batchelor, B.C. Sih, Z.-G. Ye and D.B. Leznoff, *Chem. Mater.*, 2003, **15**, 1612; D.B. Leznoff, N.D. Draper and R.J. Batchelor, *Polyhedron*, 2003, **22**, 1735; N.D. Draper, R.J. Batchelor and D.B. Leznoff, *Cryst. Growth Des.*, 2004, **4**, 621; N.D. Draper, R.J. Batchelor, P.M. Aguiar, S. Kroeker and D.B. Leznoff, *Inorg. Chem.*, 2004, **43**, 6557
- 23 C.J. Shorrock, H. Jong, R.J. Batchelor and D.B. Leznoff, *Inorg. Chem.*, 2003, **42**, 3917
- 24 B.F. Hoskins, R. Robson and N.V.Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **11**, 1203; I.K. Chu, I.P.Y. Shek, K.W.M. Siu, W.-T. Wong, J.-L. Zuo and T.-C. Lau, *New J. Chem.*, 2000, **24**, 765; E. Colacio, F. Lloret, R. Kivekas, J. Suarez-Varela, M.R. Sundberg, R. Uggla, *Inorg. Chem.*, 2003, **42**, 560; W. Dong, L.-N. Zhu, Y.-Q. Sun, M. Liang, Z.-Q. Liu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and P. Cheng, *Chem. Commun.*, 2003, 2544; S.C. Abrahams, L.E. Zyontz, J.L. Bernstein, *J. Chem. Phys.*, 1982, **76**, 5458; S.C. Abrahams, J.L. Bernstein, R. Liminga, E.T. Eisenmann, *J. Chem. Phys.*, 1980, **73**, 4585; Z. Assefa, G. Shankle, H.H. Patterson, R. Reynolds, *Inorg. Chem.*, 1994, **33**, 2187; Z. Assefa, H.H. Patterson, *Inorg. Chem.*, 1994, **33**, 6194
- 25 M. Stender, R.L. White-Morris, M.M. Olmstead and A.L. Balch, *Inorg. Chem.*, 2003, **42**, 4504
- 26 P. Güttlich, Y. Garcia and H.A. Goodwin, *Chem. Soc. Rev.*, 2000, **29**, 419; J.A. Real, A.B. Gaspar, V. Niel and M.C. Muñoz, *Coord. Chem. Rev.*, 2003, **236**, 121
- 27 A. Galet, M.C. Muñoz, V. Martinez, J.A. Real, *Chem. Commun.*, 2004, 2268; V. Niel, M.C. Muñoz, A.B. Gaspar, A. Galet, G. Levchenko and J.A. Real, *Chem. Eur. J.*, 2002, **8**, 2446; V. Niel, A.L. Thompson, M.C. Muñoz, A. Galet, A.E. Goeta and J.A. Real, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 3759
- 28 E. Colacio, F. Lloret, R. Kivekas, J. Ruiz, J. Suarez-Varela and M.R. Sundberg, *Chem. Commun.*, 2002, 592
- 29 H.-B. Zhou, S.-P. Wang, W. Dong, Z.-Q. Liu, Q.-L. Wang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and P. Cheng, *Inorg. Chem.*, 2004, **43**, 4552
- 30 D.B. Leznoff, C. Rancurel, J.-P. Sutter, S.J. Rettig, M. Pink, C. Paulsen and O. Kahn, *J. Chem. Soc., Dalton Trans.*, 1999, 3593; H. Imai, T. Otsuka, T. Naito, K. Awaga and T. Inabe, *J. Am. Chem. Soc.*, 1999, **121**, 8098
- 31 R.L. White-Morris, M.M. Olmstead, F. Jiang, D.S. Tinti and A.L. Balch, *J. Am. Chem. Soc.*, 2002, **124**, 2327; M.A. Mansour, W.B. Connick, R.J. Lachicotte, H.J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329
- 32 J. Fernandez Eduardo, J.M. Lopez-De-Luzuriaga M. Monge, M.E. Olmos, J. Perez, A. Laguna, A. Mohamed Ahmed and J.P. Fackler, Jr., *J. Am. Chem. Soc.*, 2003, **125**, 2022
- 33 M.A. Rawashdeh-Omary, M.A. Omary, J.P. Fackler, Jr., R. Galassi, B.R. Pietroni and A. Burini, *J. Am. Chem. Soc.*, 2001, **123**, 9689
- 34 C. Bariain, I.R. Matias, I. Romeo, J. Garrido and M. Laguna, *Appl. Phys. Lett.* 2000, **77**, 2274
- 35 J. Lefebvre, R.J. Batchelor and D.B. Leznoff, *J. Am. Chem. Soc.*, 2004, **126**, 16117
- 36 R.A. Penneman and R.R. Ryan, *Acta Crystallogr.*, 1972, **B28**, 1629
- 37 C. Bertinotti and A. Bertinotti, *Acta Crystallogr.*, 1970, **B26**, 422
- 38 D.M. Roundhill, In *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard, J.A. McCleverty Eds., Pergamon Press: Oxford, 1987, **5**, 351; I. Escorihuela, L.R. Falvello and M. Tomás, *Inorg. Chem.*, 2001, **40**, 636; K. Sakai, E. Ishigami, Y. Konno, T. Kajiwarra and T. Ito, *J. Am. Chem. Soc.*, 2002, **124**, 12088
- 39 L.R. Falvello and M. Tomás, *Chem. Commun.*, 1999, 273
- 40 L.R. Falvello, R. Garde, and M. Tomás, *J. Cluster Sci.*, 2000, **11**, 125
- 41 P. Vitoria, I. Muga, J.M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, F.J. Zúñiga, J.I. Beitia, *Inorg. Chem.*, 2003, **42**, 960